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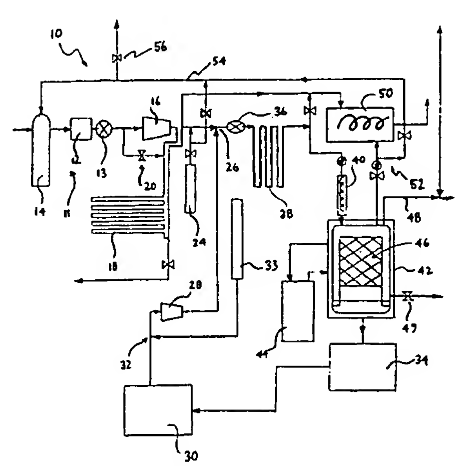
(54) Title: PRODUCTION PLANT FOR NATURAL GAS HYDRATE



(57) Abstract: A natural gas hydrate production plant (10) comprising a natural gas inlet (11), a water inlet (26), a flow path (38) and an outlet (40). The natural gas inlet (11) delivers pressurised natural gas to the flow path (38) and the water inlet (26) delivers pressurised water to the flow path (38). The flow path (38) comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions such that passage of the pressurised natural gas and water through the flow path (38) mixes the water and natural gas before the water natural gas mixture is expelled through the outlet (40), and the temperature of the water and natural gas reduced, to produce natural gas hydrate.

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PRODUCTION PLANT FOR NATURAL GAS HYDRATE

Field Of The Invention

The present invention relates to a production plant. More particularly, the present invention relates to a production plant for the production of natural gas hydrates.

Background Art

Natural gas hydrates are a stable solid comprising water and natural gas, and have been known to scientists for some years as a curiosity. More recently, natural gas hydrates have become known as a nuisance if not a serious concern in the transportation and storage of liquefied natural gas, particularly in cold climates. This has been due to the tendency of hydrates to form in pipelines thereby blocking the flow of liquefied natural gas through the pipelines.

Natural gas hydrates are formed as a result of the combination of water and gas at relatively moderate temperatures and pressures, with the resulting solid having the outward characteristics of ice, being either white or grey in colour and cold to the touch. At ambient temperatures and pressures natural gas hydrates break down releasing natural gas.

It has now been realised that natural gas hydrates can have a variety of diverse applications, including as a means for enabling the convenient transport and storage of natural gas. It is one object of the present invention to provide a production plant for the convenient manufacture of natural gas hydrates.

Known means for the manufacture of gas hydrates involve conventional refrigeration techniques. Conventional refrigeration is energy intensive and adds significantly to the cost of hydrate production. Further, the mixing of natural gas with an aqueous phase is of critical importance in the production of natural gas hydrates. Various devices for the mixing of liquid phases exist. However, many of these devices are complicated, and would add significantly to the capital and operating cost of any plant in which they are utilised. It is a further object of the

present invention to provide a production plant that minimises the use of cost intensive mixing devices. It is a secondary object of the present invention to provide a production plant that also minimises the use of cost intensive refrigeration devices.

The preceding discussion of the background to the invention is intended to facilitate an understanding of the present invention only. It should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date of the application.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

Disclosure of the Invention

Accordingly, the present invention resides in a natural gas hydrate production plant comprising a natural gas inlet, a water inlet, a flow path and an outlet, the natural gas inlet delivering pressurised natural gas to the flow path and the water inlet delivering pressurised water to the flow path, wherein the flow path is convoluted such that passage of the pressurised natural gas and water through the flow path mixes the water and natural gas before the water natural gas mixture is expelled through the outlet, and the temperature of the water and natural gas reduced, to produce natural gas hydrate.

Preferably, the flow path comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions.

Accordingly, the present invention resides in a natural gas hydrate production plant comprising a natural gas inlet, a water inlet, a flow path and an outlet, the natural gas inlet delivering pressurised natural gas to the flow path and the water

inlet delivering pressurised water to the flow path, wherein the flow path comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions such that passage of the pressurised natural gas and water through the flow path mixes the water natural and gas before the water natural gas mixture is expelled through the outlet, and the temperature of the water and natural gas reduced, to produce natural gas hydrate.

Preferably, the water and natural gas mixture is equilibrated or substantially equilibrated before being expelled through the outlet.

Without wishing to be bound by theory, it is believed that the flow path is particularly effective at mixing the water and natural gas, as the water, being more dense than the natural gas, tends to reside longer in the lower portions of the flow path whilst the lighter natural gas is forced therethrough.

In one form of the invention, the flow path is of a swirling configuration. More specifically, the flow path may be of a spiral configuration. In a highly specific form of the invention, the flow path is provided in the form of a horizontal helical spiral.

In an alternate form of the invention, the flow path is of a substantially sinusoidal configuration.

According to a preferred feature of the invention, the flow path is adapted to provide a turbulent flow. According to a preferred feature of the invention, the turbulent flow is such that the dominant velocity component is in the azimuthal direction.

In one form of the invention, the flow path is provided with internal means to impart a spiralling motion to the water and natural gas flowing therethrough. In a specific form of the invention, the flow path is internally rifled.

In one embodiment of the invention, the flow path is provided in the form of a length of wide-bore piping.

In a preferred characteristic of the production plant that the residence time of the natural gas and water in the flow path is at least one minute.

A mixing apparatus may be provided immediately upstream of the flow path to produce an intimate admixture of water and natural gas. In one form of the invention, a corrugated mixer is provided immediately upstream from the convoluted flow path.

Preferably, the outlet is adapted to mediate a rapid pressure reduction of the water and natural gas as it is expelled therethrough.

Preferably, the outlet mediates a reduction in pressure from at least 70 bar to near atmospheric pressure. Preferably still, the outlet mediates a reduction in pressure from in excess of about 140 bar to near atmospheric pressure. In a specific form of the invention, the outlet mediates a decrease in pressure from about 145 bar to near atmospheric pressure. In one form of the invention, the outlet is provided in the form of a Joule-Thompson nozzle.

In a preferred form of the invention, the outlet is heated to reduce the possibility of blockage.

Preferably, the outlet finely divides the water and natural gas as it is expelled therethrough. Preferably still, the outlet atomises the water and natural gas as it is expelled therethrough.

According to a preferred feature of the invention, the production plant still further comprises an additive introduction assembly for the introduction of additives beneficial to the formation of natural gas hydrates to the process stream.

According to a preferred feature of the invention, the production plant further comprises a capture vessel to receive the output from the outlet. According to a preferred feature of the invention, the capture vessel is maintained at a reduced temperature.

According to a further preferred feature of the invention, the capture vessel comprises a collection means for collecting hydrate. According to one embodiment, the collecting means is, formed from a screening medium adapted to retain solid material whilst allowing fluid material to pass therethrough.

The invention also resides in a method of forming natural gas hydrates, the method comprising the steps of:-

introducing water and natural gas into a flow path at elevated pressure wherein the flow path comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions such that passage of the pressurised natural gas and water through the flow path mixes the water and natural gas; and

expelling the mixture of natural gas and water from the flow path through an outlet and reducing the temperature of the mixture of natural gas and water to form natural gas hydrate.

According to a preferred form of the invention, passage of the natural gas and water through the flow path causes the mixture of such to equilibrate or substantially equilibrate.

According to a preferred feature of the invention, the outlet is adapted to mediate a rapid pressure reduction, thereby reducing the temperature of the natural gas water mixture.

According to a preferred embodiment of the invention, the gas and water are mixed at pressures exceeding approximately 70 bar. Preferably still, the gas and water are mixed at pressures exceeding approximately 140 bar. In one form of the invention, the gas and water are mixed at a pressure approximating 145 bar. According to a further preferred embodiment of the invention, the outlet mediates a decrease in pressure to approximately near atmospheric pressure.

The method of the present invention may comprise the additional step of introducing one or more additives to the flow path and mixing the natural gas, the

water and the or each additive. Preferably, the mixture is caused to substantially equilibrate or equilibrate.

As hydrate is formed, the pressure differential across the Joule-Thompson nozzle may decrease, particularly when the Joule-Thompson nozzle is in communication with a closed capture vessel. Accordingly, where the method of the present invention is employed by way of a production plant incorporating a heated Joule-Thompson nozzle, the method of the present invention may comprise the additional step of:

varying the temperature of the Joule-Thompson nozzle in inverse proportion to the pressure in the capture vessel.

The best modes of carrying out the invention presently known to the applicant will now be described with reference to three specific embodiments of the invention.

Brief Description of the Drawing

The description of the embodiments is made with reference to the accompanying drawings, in which:

Figure 1 is a schematic representation of a plant according to the first embodiment; and

Figure 2 is a representation of an extended, convoluted flow path according to the embodiments.

Best Mode(s) For Carrying Out The Invention

Figure 1 shows a schematic illustration of a natural gas hydrate production plant 10 according to the embodiment, for producing natural gas hydrates according to the method of the embodiment.

The production plant 10 comprises an inlet 11 incorporating an in-line gas filter in the form of an activated carbon filter 12, a regulator 13 and a liquid knock out

vessel 14. A supply of natural gas is introduced through the liquid knockout vessel 14 and the activated carbon filter 12, thereby removing liquid and non-liquid impurities therefrom.

The pressure of the natural gas is increased to about 145 bar by way of a gas pressurising means in the form of a compressor 16. To counteract the heating effect associated with compression, the gas is then passed through a cooling coil 18. A by-pass valve 20 allows gas to be passed directly to the cooling coil 18, and a ventilation valve 22 allows gas to be ventilated directly from the cooling coil 18 to the environment.

A high-pressure gas storage vessel 24 is located immediately downstream from the cooling coil 18.

The production plant 10 further comprises a water inlet, incorporating a joining tee 26, and a liquid pressure booster in the form of a pump 28. The joining tee 26 is adapted to deliver water downstream from the cooling coil 18, and immediately downstream from the high pressure gas storage vessel 24. The pump 28 is in communication with a water supply 30 and, in cooperation with the joining tee 26, ensures that water is introduced downstream from the cooling coil 18 at elevated pressure.

In controlled communication with the water supply 30, upstream from the liquid pressure booster 28, is an additive inlet 32 in communication with an additive source 33. The additive inlet 32 and the additive source introduce additives beneficial to the production of natural gas hydrates, such as those described in our co-pending application entitled "Natural Gas Hydrate And Method For Producing Same" to the water supply to create an additive-water mixture.

A water monitoring system 34 is further provided and is capable of measuring water salinity and water pH, and is used to monitor the production plant 10 of the embodiment.

The additive-water mixture is introduced to the cooled, compressed natural gas downstream from the high pressure gas storage vessel 24, and immediately upstream from a mixing apparatus in the form of a corrugated mixer 36.

Having passed through the corrugated mixer 36, the water-additive-gas stream flows to a flow path in the form of a length of wide bore piping 38, where the water-additive-gas stream is substantially equilibrated. As can be seen in Figure 2, the wide bore piping 38 is of a substantially sinusoidal configuration, having high portions 38a, and low portions 38b.

Without wishing to be bound by theory, it is believed that the wide bore piping 38 is particularly effective at mixing the water and natural gas as the water, being more dense than the liquefied gas, tends to reside longer in the low portions 38b whilst the lighter gas component is forced therethrough.

The wide bore piping 38 slows the flow of the water-additive-gas stream, increasing residence times allowing more effective mixing. In the embodiment, the wide bore piping 38 is of a length and diameter to provide a residence time of approximately one minute.

The substantially equilibrated gas-additive-water mixture, at a pressure of approximately 145 bar is then forced through an outlet adapted to atomise and to mediate a reduction in the pressure of the gas-additive-water mixture to near atmospheric pressure, in the form of a heated Joule-Thompson nozzle 40. The rapid pressure reduction causes rapid cooling, and the production of natural gas hydrate.

The production plant 10 further comprises a capture vessel 42 in communication with the Joule-Thompson nozzle 40, the capture vessel 42 being maintained at a temperature of approximately –6°C by way of a refrigeration unit 44, whilst the Joule-Thompson nozzle 40 is initially maintained at a temperature of approximately 65°C. The capture vessel 42 in turn comprises a separation means for separating hydrate from unreacted gas in the form of an intermediate vessel 46 of mesh, adapted to retain solid material whilst allowing fluid to pass

therethrough. The capture vessel is further provided with an automated over pressure relief valve 48, and a manual pressure adjustment valve 49.

As the hydrate is formed, the pressure inside the capture vessel 42 increases. Accordingly, the pressure drop across the Joule-Thompson nozzle 40 decreases. Allowance for the decrease in pressure differential is made by steadily decreasing the temperature of the Joule-Thompson nozzle 40 as the hydrate is formed.

With the rapid reduction in pressure, any unreacted natural gas resumes a gaseous state, and is readily separated from unreacted water. The unreacted water may be sampled by way of the water monitoring means 34.

The production plant 10 further comprises a gas monitoring means in the form of a gas chromatograph 50 and a sampling means 52. The unreacted gas may be sampled, from the capture vessel 42 by way of the sampling means 52, and analysed by the gas chromatograph 50. Typically however, the unreacted gas is recycled to the liquid knockout vessel 14, by way of a gas return line 54. The gas return line 54 is provided with a manual pressure adjustment means 56.

Should it be necessary to depressurise the production plant 10 of the embodiment, the high-pressure gas storage vessel 24 is intended to assist in restoring the production plant 10 to operating pressure. The high-pressure gas storage vessel 24 stores gas pressurised by the compressor 16. Once the production plant 10 is resealed after depressurisation, the contents of the high-pressure gas storage vessel 24 may be released to assist in the re-pressurisation of the plant 10, considerably reducing down-time.

In accordance with a second embodiment of the invention, there is provided a production plant (not shown). The production plant of the second embodiment is similar to the production plant 10. However, the capture vessel of the production plant of the second embodiment is adapted to maintain a substantially constant pressure.

In accordance with a third embodiment of the invention, there is provided a production plant (not shown). The production plant of the third embodiment is similar to the production plant 10 and the production plant of the second embodiment. However the capture vessel of the production plant of the third embodiment is adapted to maintain a pressure that varies periodically between an upper level and a lower level.

Modifications and variations as would be apparent to the skilled addressee are considered to fall within the scope of this invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1. A natural gas hydrate production plant comprising a natural gas inlet, a water inlet, a flow path and an outlet, the natural gas inlet delivering pressurised natural gas to the flow path and the water inlet delivering pressurised water to the flow path, wherein the flow path is convoluted such that passage of the pressurised natural gas and water through the flow path mixes the water natural and gas before the water natural gas mixture is expelled through the outlet, and the temperature of the water and natural gas reduced, to produce natural gas hydrate.

2. A natural gas hydrate production plant according to claim 1 characterised in that the flow path comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions.

3. A natural gas hydrate production plant comprising a natural gas inlet, a water inlet, a flow path and an outlet, the natural gas inlet delivering pressurised natural gas to the flow path and the water inlet delivering pressurised water to the flow path, wherein the flow path comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions such that passage of the pressurised natural gas and water through the flow path mixes the water natural and gas before the water natural gas mixture is expelled through the outlet, and the temperature of the water and natural gas reduced, to produce natural gas hydrate.

4. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the water and natural gas mixture is equilibrated or substantially equilibrated before being expelled through the outlet.

5. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the flow path is of a swirling configuration.

6. A natural gas hydrate production plant according to claim 5 characterised in that the flow path is of a spiral configuration.

7. A natural gas hydrate production plant according to claim 6 characterised in that the flow path is provided in the form of a horizontal helical spiral.

8. A natural gas hydrate production plant according to any of claims 1 to 4 characterised in that the flow path is of a substantially sinusoidal configuration.

9. A natural gas hydrate production plant according to any one of the preceding claims, characterised in that the flow path is adapted to provide a turbulent flow.

10. A natural gas hydrate production plant according to claim 9, characterised in that the turbulent flow is such that the dominant velocity component is in the azimuthal direction.

11. A natural gas hydrate production plant according to claim 9 or 10 characterised in that the flow path is provided with internal means to impart a spiralling motion to the water and natural gas flowing therethrough.

12. A natural gas hydrate production plant according to claim 11 characterised in that the flow path is internally rifled.

13. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the flow path is provided in the form of a length of wide-bore piping.

14. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the residence time of the natural gas and water in the flow path is at least one minute.

15. A natural gas hydrate production plant according to any one of the preceding claims characterised in that a mixing apparatus is provided immediately

upstream of the flow path to produce an intimate admixture of water and natural gas.

16. A natural gas hydrate production plant according to claim 15 characterised in that the mixing apparatus is provided in the form of a corrugated mixer.

17. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the outlet is adapted to mediate a rapid pressure reduction of the water and natural gas as it is expelled therethrough.

18. A natural gas hydrate production plant according to claim 17 characterised in that the outlet mediates a reduction in pressure from at least 70 bar to near atmospheric pressure.

19. A natural gas hydrate production plant according to claim 18 characterised in that the outlet mediates a reduction in pressure from in excess of about 140 bar to near atmospheric pressure.

20. A natural gas hydrate production plant according to claim 19 characterised in that the outlet mediates a decrease in pressure from about 145 bar to near atmospheric pressure.

21. A natural gas hydrate production plant according to any one of claims 17 to 20 characterised in that the outlet is provided in the form of a Joule-Thompson nozzle.

22. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the outlet finely divides the water and natural gas as it is expelled therethrough.

23. A natural gas hydrate production plant according to claim 22 characterised in that the outlet atomises the water and natural gas as it is expelled therethrough.

24. A natural gas hydrate production plant according to any one of claims 17 to 23 characterised in that the outlet is heated to reduce the possibility of blockage.

25. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the production plant comprises an additive introduction assembly for the introduction of additives beneficial to the formation of natural gas hydrates to the process stream.

26. A natural gas hydrate production plant according to any one of the preceding claims characterised in that the production plant comprises a capture vessel to receive the output from the outlet.

27. A natural gas hydrate production plant according to claim 26 characterised in that the capture vessel is maintained at a reduced temperature.

28. A natural gas hydrate production plant according to claim 26 or 27 characterised in that the capture vessel comprises a collection means for collecting hydrate.

29. A natural gas hydrate production plant according to claim 26 characterised in that the collecting means is, formed from a screening medium adapted to retain solid material whilst allowing fluid material to pass therethrough.

30. A method of forming natural gas hydrates comprising the steps of:-

introducing water and natural gas into a flow path at elevated pressure wherein the flow path comprises a plurality of first portions alternating with a plurality of second portions, the second portions being located at a lower level than the first portions such that passage of the pressurised natural gas and water through the flow path mixes the water and natural gas; and

expelling the mixture of natural gas and water from the flow path through an outlet and reducing the temperature of the mixture of natural gas and water to form natural gas hydrate.

31. A method according to claim 30 characterised in that passage of the natural gas and water through the flow path causes the mixture of such to equilibrate or substantially equilibrate.

32. A method according to claim 30 or 31 characterised in that the outlet is adapted to mediate a rapid pressure reduction of the water and natural gas, thereby reducing the temperature of the natural gas water mixture.

33. A method according to any one of claims 30 to 31 characterised in that the natural gas and water are mixed at pressures exceeding approximately 70 bar.

34. A method according to claim 33 characterised in that the natural gas and water are mixed at pressures exceeding approximately 140 bar.

35. A method according to claim 34 characterised in that the natural gas and water are mixed at a pressure approximating 145 bar.

36. A method according to any one of claims 30 to 35 characterised in that the outlet mediates a decrease in pressure to near atmospheric pressure.

37. A method according to any one of claims 30 to 36 characterised by the step of finely dividing the water and natural gas as they are expelled through the outlet.

38. A method according to any one of claims 30 to 37 characterised by the step of atomising the water and natural gas as they are expelled through the outlet.

39. A method according to any one of claims 30 to 38 characterised in that the method comprises the additional step of introducing one or more additives to the flow path and mixing the natural gas, the water and the or each additive.

40. A method according to claim 39 characterised in that the mixture is caused to substantially equilibrate or equilibrate.

41. A method according to any one of claims 30 to 40 characterised in that the method comprises the step of:

    varying the temperature of the Joule-Thompson nozzle in inverse proportion to the pressure in the capture vessel.

42. A natural gas hydrate production plant substantially as described herein with reference to Figures 1 and 2.

43. A method of forming natural gas hydrates substantially as described herein with reference to Figures 1 and 2.

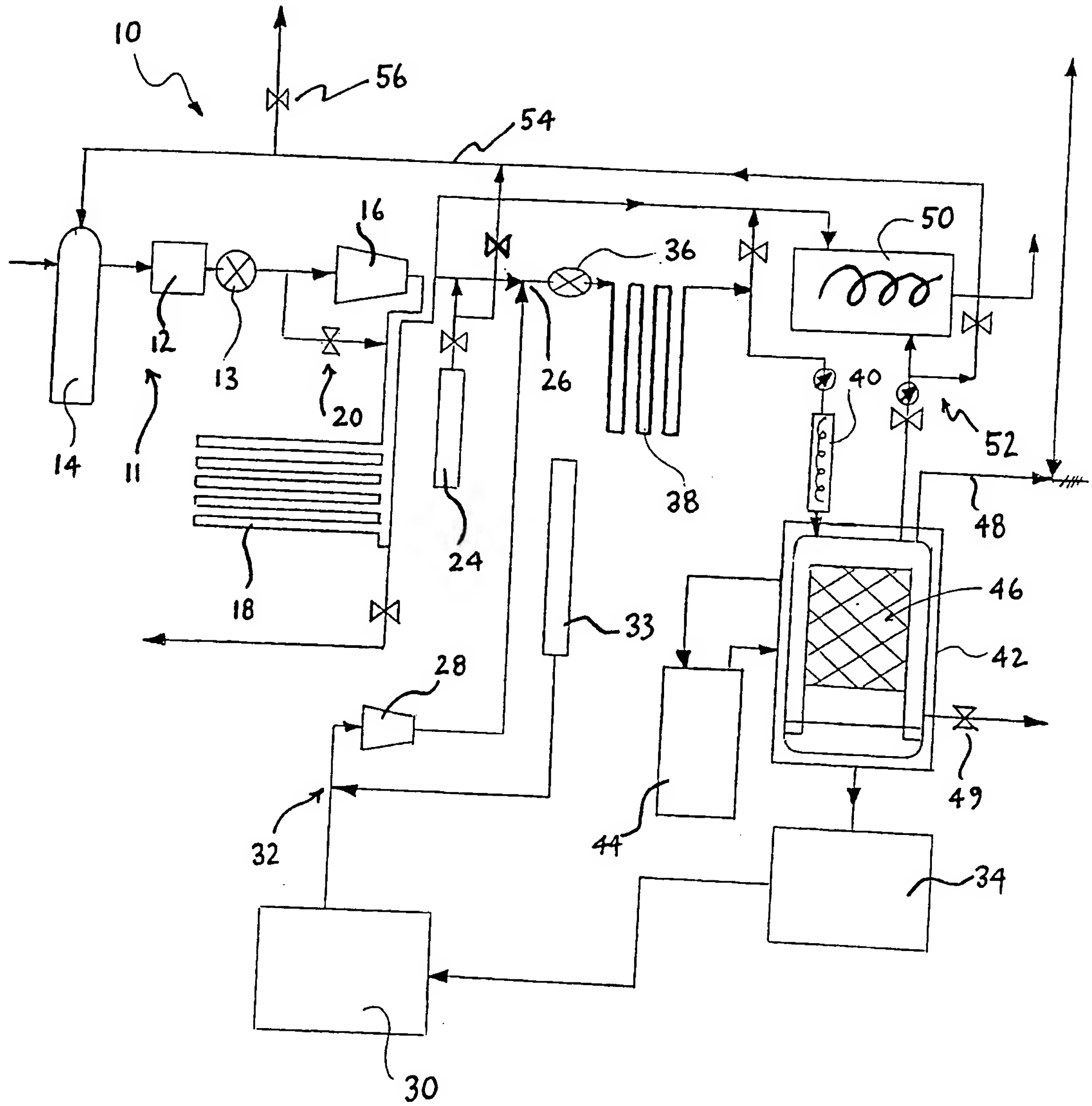
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Fig. 1

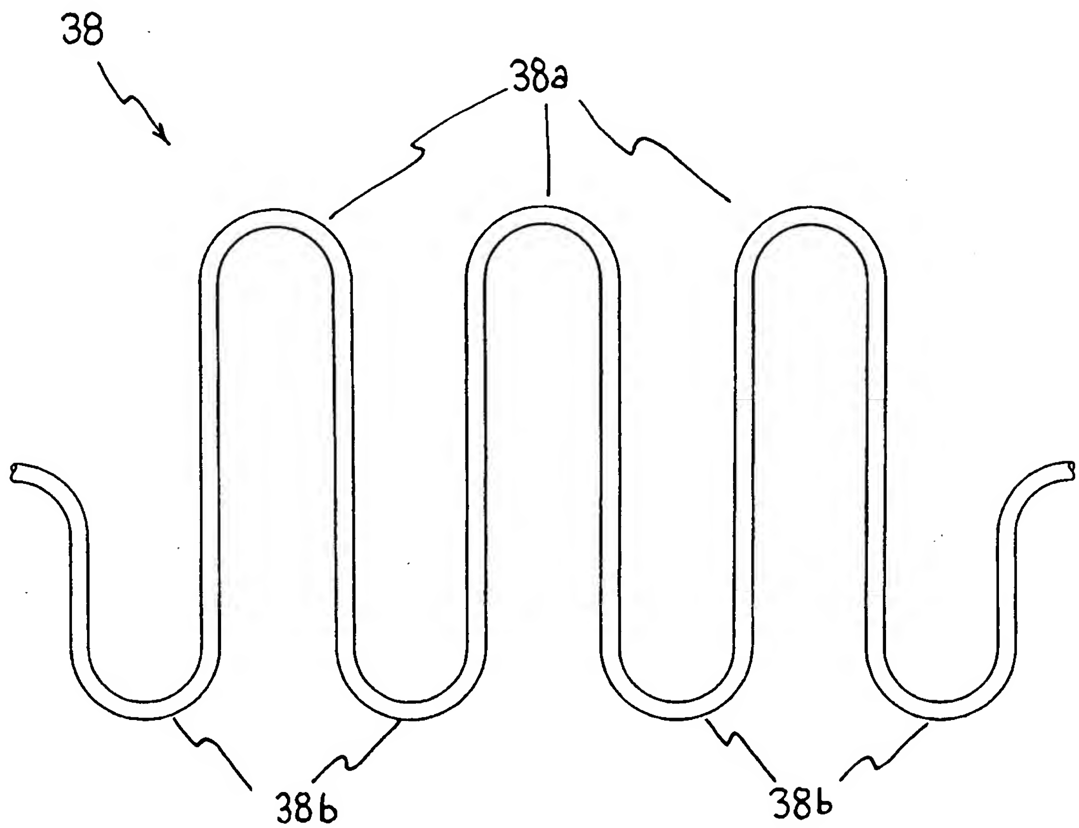

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/00973

A. CLASSIFICATION OF SUBJECT MATTER	
Int. Cl. 7:	C10L 3/06, B01F 5/00, B01J 19/24

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L 3/06, B01F 3/04, 5/00, B01J 19/24, 10/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU:IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT:(HYDRATE+ or CLATHRATE+)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 309 227 A (BRITISH GAS PLC) 23 July 1997 See page 4 lines 4 to 27 and Figures 2-4.	1
X	US 3 514 274 A (Cahn et al.) 26 May 1970 See the Abstract, column 3 lines 52 to 65 and Figure 1.	1
A	WO 93 01153 A (Gudmundsson) 21 January 1993	

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 9 October 2000	Date of mailing of the international search report 12 OCT 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer JOHN DEUIS Telephone No : (02) 6283 2146

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/00973

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
GB	2309227	AU	13865/97	CA	2214373	CN	1181806
		DK	1007/97	EP	820574	NZ	325367
		PL	322305	US	6111155	WO	9726494
US	3514274	NONE					
WO	9301153	EP	594616	NO	900395	NO	9000395

END OF ANNEX